

## **A Chemical Percolation Model for Devolatilization: Temperature and Heating Rate Effects\***

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### **INTRODUCTION**

It is well known that the yield of volatile matter obtained from a pulverized coal is dependent upon the temperature history of the particle. However, the effect of heating rate on volatiles yield is difficult to study independently of final temperature. For example, the volatile yields obtained in an entrained flow reactor study by Kobayashi, et al. [1] increase with both temperature and heating rate, but the independent contribution of heating rate could not be assessed. Heated screen experiments were developed to study devolatilization behavior at different heating rates independently from the final particle temperature. The data of Anthony and Howard [2] show little increase in volatiles yield when particles are heated to the same final temperature on a heated screen at different heating rates. In a more recent study, Gibbins-Matham and Kandiyoti [3] show evidence for small increases in the volatiles yield from a Pittsburgh #8 coal as the heating rate is increased from 1 K/s to 1000 K/s on a heated screen. Coal samples were heated at 5 different heating rates to a final temperature of 700°C and held for 30 s. Experiments were repeated several times in order to ensure accuracy of the data. The total volatiles yield increases from 41.5% at 1 K/s to 46.8% at 1000 K/s, a relative increase in yield of 13%. This increase in yield with increase in heating rate is small, but is larger than associated experimental errors.

The chemical percolation devolatilization (CPD) model [4] was developed as a means to describe coal devolatilization behavior based upon the chemical structure of the parent coal. Some of the input parameters for this model are obtained from NMR characterizations of the parent coal. Percolation statistics are used to describe the probability of generating finite tar fragments from the infinite coal matrix. Pyrolysis yields of tar, gas, and char for three different types of coal are described using a single set of kinetic parameters; only chemical structure parameters are changed for the different coals. The initial description of the CPD model [4] allowed for a temperature dependence of the competition between side chain formation and char formation. However, this option was not exercised in the initial study in order to demonstrate general utility of the model for one set of devolatilization data on three coals collected over a narrow range of temperatures and heating rates. In the present work, the Gibbins-Matham and Kandiyoti data are used to determine additional coefficients for the CPD model that accurately predict the changes in char and tar yield as a function of heating rate.

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## THEORY

### The Chemical Percolation Devolatilization Model

Coal is treated in the CPD model as a macromolecular array of clusters representing the interconnections of aromatic ring structures of various sizes and types. These clusters are connected by a variety of chemical bridges of different bond strengths. Percolation statistics applicable to a Bethe lattice (a loopless tree structure) allow a mathematical description of the bridge-breaking process in closed form, providing an efficient alternative to Monte-Carlo techniques. Tar is formed as finite aromatic clusters separate from the infinite coal lattice. Labile bridges  $L$  decompose into a reactive intermediate  $L^*$ , as follows:



The reactive intermediate is unstable, and reacts quickly in a competitive reaction sequence. In one reaction pathway, the reactive intermediate may recombine to form a stable char bridge  $c$  with the associated release of light gas  $g_2$ :



In a competing reaction pathway, the reactive intermediate is stabilized and forms side chains  $\delta$  (rather than recombining to form char):



The cleavage of the reactive intermediate in this step constitutes the bridge-breaking step, and is tied to the generation of tar fragments through percolation statistics. The side chains eventually react to form light gas  $g_1$ :



The competition for  $L^*$  is governed by the ratio of the rate of side chain formation to the rate of char formation, and it is convenient to define a composite rate constant  $p$ :

$$p = \frac{k_\delta}{k_c} = \frac{A_\delta}{A_c} \exp\left[\frac{-(E_\delta - E_c)}{RT}\right] = A_p \exp\left[\frac{-E_p}{RT}\right] \quad (5)$$

The dynamic variables of the theory are the bridge population parameters,  $L$  and  $c$ , and the chain fragment parameter  $\delta$ . A steady-state approximation is invoked for the reactive intermediate  $L^*$  (i.e.,  $dL^*/dt = 0$ ), yielding differential expressions for the reaction rates of  $L$ ,  $c$ , and  $\delta$  [4].

### Modifications to the CPD Model

In the initial formulation of the CPD model [4], the temperature dependence of  $p$  was neglected by setting  $E_p$  to zero and adjusting  $A_p$  to match the experimental data. This approach was sufficient to allow determination of an effective rate coefficient  $p$  that explained the pyrolysis behavior of a limited set of data with a well-characterized temperature history obtained for three different coals

at one heating rate [5]. Measurements of the devolatilization rate performed recently at Sandia [6] include single particle temperature measurements, and show general agreement with the rates obtained by Serio, et al. [5]. In a subsequent study, the sensitivity of the CPD model to nonzero values of  $E_p$  was explored, and it was shown that the total yield predicted by the model changes as a function of heating rate, as expected. However, sensitivity studies show that regardless of the value of  $E_p$ , the model cannot accurately predict tar yields over a wide range of heating rates. Physical mechanisms that limit the production of tar were therefore considered that would allow more realistic predictions using the CPD model.

The ratio of the tar yield to the char yield is affected by the amount of hydrogen in the coal. For example, in the limiting case, anthracites contain little hydrogen, and hence release little volatile matter. All of the hydrogen in the coal, however, is not available to support the release of tar during devolatilization. In some coals, a considerable amount of hydrogen is contained in aliphatic groups, such as methyl ( $-CH_3$ ) groups, which are released in the form of light gases rather than combining with larger reactive molecules to produce volatile tars. The amount of available hydrogen for tar stabilization is therefore not directly related to the total amount of hydrogen present in the coal. The amount of available hydrogen for tar formation has been used in several recent coal devolatilization models [7,8]. At present, quantitative experimental methods for measuring the amount of hydrogen available for stabilization of reactive intermediates that lead to tar are not available.

In the CPD model, production of tar can be limited by introduction of a variable to represent the amount of hydrogen available for stabilization of the reactive intermediate  $L^*$ . To include the available hydrogen  $h$  explicitly in the reaction sequence, Eq. 3 is modified as follows:



Here  $h$  is normalized by the total possible number of bridges in the lattice (the same basis as  $L$ ). As  $h$  is depleted, the reactive intermediate is no longer able to form side chains, causing preferential formation of char. This equation becomes a bimolecular reaction, rather than a unimolecular decomposition reaction (Eq. 3), with an overall reaction order of two rather than one. The reaction rate for  $L$  is unchanged, but the reaction rates for  $c$  and  $\delta$  include the term  $ph$  instead of  $p$ . In addition, the reaction rate of  $h$  is formulated as follows:

$$\frac{dh}{dt} = -k_\delta L^* h = -\frac{k_\delta k_p L h}{k_c + k_\delta h} = -\frac{k_b \rho h L}{1 + \rho h} \quad (7)$$

where  $\rho$  is defined in Eq. 5. The variable  $h$  is highly coupled to the composite rate constant  $\rho$ , evidenced by the fact that  $\rho$  and  $h$  appear together in all of the equations except in the derivative term  $dh/dt$  in Eq. 7. As discussed later, this high degree of coupling restricts independent evaluation of  $\rho$  and the initial amount of available hydrogen  $h_0$  using experimentally measured release rates of tar and total volatiles. The method of relating the production of finite clusters to the number of intact bridges remains unchanged by the introduction of the variable  $h$ ; the mass fractions of tar, gas, and char are therefore calculated as a function of the dynamic variables  $L$ ,  $c$ , and  $\delta$  [4].

## DISCUSSION

Coal specific parameters for the CPD model are ideally obtained from independent chemical analyses, such as NMR characterizations [9]. In practice, the NMR data can only guide the

selection of coal specific parameters such as the coordination number ( $\sigma+1$ ), the initial fraction of intact bridges  $p_0$ , the initial fraction of char bridges  $c_0$ , and the ultimate gas yield  $f_\infty$ . Refinements of these structural parameters are obtained from least squares fits of experimentally measured rates and yields of tar and total volatiles. The kinetic parameters used by the model are assumed to be coal independent, and these parameters were previously obtained [4] by comparison with data [5].

#### Determination of Structural Parameters for Pittsburgh #8 Coal

The coal investigated by Gibbins-Matham and Kandiyoti [3] was a Pittsburgh #8 hva bituminous coal. The results of Serio, et al. [5] for three different coals (Illinois #6 hvb bituminous, Montana Rosebud, and North Dakota Beulah Zap lignite) were previously used to set parameters for the original development of the CPD model [4], but data were unavailable for Pittsburgh #8 coal. A Pittsburgh #8 coal (PSOC-1451D) was investigated by Fletcher [6] and by Freihaut [10]. Based on the devolatilization rates obtained by Fletcher [6] which include single particle temperature measurements, the heated screen experiments performed by Gibbins-Matham and Kandiyoti and by Freihaut appear to have reasonable estimates of particle temperature during devolatilization. The tar and total volatiles yield data of Freihaut are therefore used to determine chemical structure parameters for the CPD model for the Pittsburgh #8 coal using the kinetic parameters from the previous study [4]. The parameters required by the CPD model that represent the chemical structure of the parent coal are the coordination number ( $\sigma+1$ ), the initial concentration of labile bridges  $L_0$ , the initial concentration of char (or refractory) bridges  $c_0$ , and the ultimate gas yield  $f_\infty$ . The coordination number ( $\sigma+1$ ) used in this study is 5.8, as determined for Pittsburgh #8 hva bituminous coal by  $^{13}\text{C}$  NMR spectroscopy and carbon-counting techniques [9].

Values for  $L_0$ ,  $c_0$ , and  $f_\infty$  are obtained from least squares fits to Freihaut's heated screen data (tar and char yields) at 1000 K/s with zero hold time at the maximum temperature. In these simulations,  $E_p$  was set to zero, and the coal was assumed to cool at 1000 K/s after the desired temperature was achieved. Results of this least squares fit are  $L_0 = 0.311$ ,  $c_0 = 0.138$ ,  $f_\infty = 0.305$ . The comparison with Freihaut's data is shown in Figure 1. The model predicts both the yield and temperature dependence of the char formation and tar release data. The fact that the predicted initial tar yield is non-zero is indicative of finite lattice clusters existing in the parent coal. A study of vaporization mechanisms of this tar precursor material is in progress.

#### Determination of $A_p$ and $E_p$

The values of  $A_p$  and  $E_p$  in this model control the temperature dependence of the competition between char formation and gas formation, which is assumed to be relatively independent of coal type. It is anticipated that  $h_0$  will be determined in the future from some type of chemical analysis of the parent coal structure, but for the present, existing methods are insufficient to determine this parameter. The experimental data on Pittsburgh #8 coal can be modeled equally well with different values of  $h_0$ , as long as  $h_0$  is large enough to permit adequate tar yields. Predicted tar yields decrease when values of  $h_0$  of 0.2 or lower are used for the Pittsburgh #8 and Illinois #6 coals, since the available hydrogen is completely consumed and side chain formation is no longer possible. For values of  $h_0$  greater than 0.25, finite concentrations of h exist after depletion of the labile bridges L, and the tar yield is not decreased. Successful CPD model predictions of the devolatilization behavior of both the Illinois #6 and Pittsburgh #8 coals can be made using values of  $h_0$  ranging from 0.25 to 0.4. Studies to determine the appropriate value of  $h_0$  as a function of coal type will be conducted in the future. For each value of  $h_0$  used, a different set of values for  $A_p$  and  $E_p$  is required to fit the Serio, et al. [5] Illinois #6 data. Since these data were obtained at

only one heating rate, there is insufficient resolution to determine both  $A_p$  and  $E_p$ . A correlation for  $A_p$  was therefore determined for different input values of  $E_p$  that best fit the Serio, et al. data. Figure 2 shows the least squares fits to the data with  $h_0 = 0.3$  and  $E_p = 3.0$  kcal/mole. The reaction histories of the dynamic variables used in this calculation are shown in Figure 3. The available hydrogen,  $h$ , is consumed rapidly as the tar is released, but a modest residual value remains when the population of labile bridges goes to zero. The reaction histories of the dynamic variables other than  $h$  ( $L$ ,  $c$ ,  $g_1$ ,  $g_2$ , and  $\delta$ ) are similar to those predicted by the original CPD model [4], and are seemingly unaffected by  $h$  except when the value selected for  $h_0$  is low enough to restrict side chain formation (and hence affect tar and gas yields).

A fitting routine was used to determine a suitable value for  $E_p$  from the data of Gibbins-Matham and Kandiyoti. The total volatiles yield measured by Gibbins-Matham and Kandiyoti differs from the yield measured by Freihaut, which is not surprising, since all Pittsburgh #8 hva bituminous coals are not identical. Therefore, only the difference in measured yields as a function of heating rate were used in the determination of  $E_p$ , thereby avoiding problems in fitting the absolute yields at each heating rate. In this numerical simulation of the experiment, particles are heated to 700°C at the specified heating rate and held at that temperature for 30 s. The fitting procedure determines the changes in total yield using the chemical structure coefficients obtained from NMR analysis [9] and least squares fit to Freihaut's data [10] ( $\sigma+1 = 5.8$ ,  $L_0 = 0.311$ ,  $c_0 = 0.138$ , and  $f_{\infty} = 0.305$ ). The only fitting parameter used to correlate the change in yield versus heating rate is  $E_p$ ;  $A_p$  is calculated from the correlation based on  $E_p$  developed from the Serio, et al. data. Results of this least squares fit are shown in Table 1 for  $h_0 = 0.3$ ,  $E_p = 3.0$  kcal/mole, and  $A_p = 26.8$  s<sup>-1</sup>. The  $\Delta V$  columns represent the difference in total volatile yield from the 1 K/s condition. The modest value determined for  $E_p$  of 3 kcal/mole is not surprising since  $E_p$  is a difference of two activation energies ( $E_\delta - E_c$ ). In contrast, the activation energy associated with labile bridge scission  $E_b$  is 55 kcal/mole [4]. Thus, the temperature dependence of side chain formation with rate  $k_\delta$  is only slightly more favorable than the temperature dependence of the rate of char formation  $k_c$  under these conditions.

Table 1  
Predicted and Measured Changes in Total Volatiles Yield  
as a Function of Heating Rate for Pittsburgh #8 Hva Bituminous Coal

Heating Rate (K/s)	Measured by [3] $\Delta V$ (%)	CPD Model $h_0 = 0.30$ $\Delta V$ (%)
1	0.0	0.0
3	- 0.7	0.6
10	2.2	1.4
100	3.0	3.3
1000	5.3	5.3

#### Extension to Other Heating Rates and Temperatures

The CPD model can be used to predict the effects of heating rate over a broader range of temperatures and heating rates using the coefficients obtained from the least squares fits to the above-mentioned data sets. Figures 4-5 show the heating rate dependence of the model for the devolatilization of Illinois #6 coal. In these calculations, the coal is heated to 1500 K at rates from 1 K/s to 10<sup>5</sup> K/s. The effect is two-fold: (a) the temperature at which the reactions occur

increases as the heating rate increases, and (b) the total volatiles yield (gas + tar) increases as the heating rate increases. The predicted change in yield with heating rate is only a function of  $E_p$ . When  $E_p = 0$ , there is no predicted difference in volatiles yield as a function of heating rate. The shift in reaction temperature with heating rate is a result of competition between the devolatilization rate and the heating rate. The competition between chemical reactions and heat transfer governs changes in reaction temperatures with heating rate. The decrease in overall tar yield at higher temperatures is due to gas phase thermal cracking, resulting in the production of light gas.

The temperature dependence of the model can be explored further by comparison with devolatilization data obtained at high heating rates and long hold times at different temperatures. Freihaut [10] performed devolatilization experiments on Pittsburgh #8 hva bituminous coal at 1000 K/s, and varied the hold time from 0 to 100 s at different temperatures. The tar yield measured at the 100 s hold time condition is much greater than the zero hold condition at any given temperature between 700 and 900 K. He postulates that additional low-temperature coking reactions are needed to model this phenomena. Using the chemical structure coefficients described above, and the values of  $E_p$  and  $A_p$  corresponding to the best fits to the Gibbins-Matham and Kandiyoti data with  $h_0 = 0.3$ , predictions of the Freihaut 100 s and 50 s hold-time data were performed using the modified CPD model (see Figure 6). The model successfully predicts both the temperature dependence of tar evolution and the increase in yield at the 100 s hold time condition. The comparison with the limited 50 s hold condition is not quite as good. It is interesting that the CPD model is able to explain these experimental data without additional low temperature reactions. In addition, the CPD model allows the tar to continue to crack and release light gas as if it were at the same temperature as the coal particle. This results in the predicted decrease in tar yield at 800 K for the 100 s hold time condition and at 1000 K for the immediate quench (zero hold time) condition.

#### SUMMARY

The chemical percolation devolatilization (CPD) model was modified to account for differences in total volatiles yield attained at different heating rates. Modifications include the addition of a new dynamic variable to account for the hydrogen available to stabilize side chains formed from reactive intermediates of labile bridge scission. The temperature dependence of the competition between side chain formation and char formation was explored in some detail and found to give rise to changing tar yields with variations in heating rate. Coefficients were developed for the resulting model based on (a) NMR data for Pittsburgh #8 hva bituminous coal [9], (b) tar and char yield data for Pittsburgh #8 coal [10], (c) kinetic rate data from an Illinois #6 hvb bituminous coal [5], and (d) volatiles yield data as a function of heating rate for a Pittsburgh #8 coal [3]. Simulations were performed to show the predicted effects of heating rate and final temperature. Successful predictions of the devolatilization behavior of the Pittsburgh #8 coal and the Illinois #6 coal were performed using values for the initial amount of available hydrogen  $h_0$  ranging from 0.25 to 0.4. Future studies will explore methods to determine a suitable value for this parameter by comparison with additional experimental data on other coals at various heating rates.

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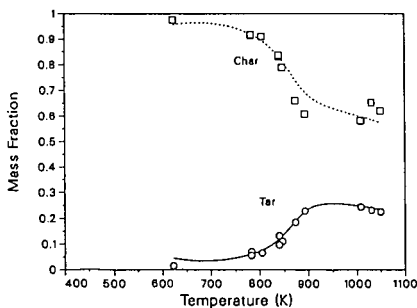


Figure 1. Results of least squares fit to Freihaut PSOC-1451D hva bituminous coal pyrolysis data [10] (points) using the CPD model (continuous lines). In Freihaut's experiment, coal particles are heated at 1000 K/s to the designated final temperature, and then cooled immediately to room temperature (zero hold time). Coefficients determined from this fit to the data are  $L_0 = 0.311$ ,  $c_0 = 0.138$ , and  $f_{\infty} = 0.305$ .

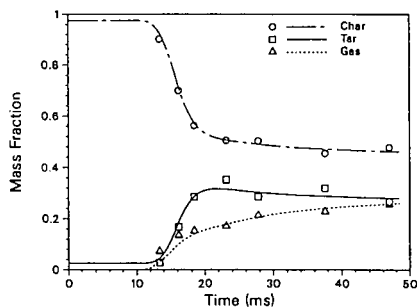


Figure 2. Results of least squares fit to Serio, et al. [5] devolatilization data (points) using the CPD model (continuous lines). In this experiment, Illinois #6 hvb bituminous coal particles are heated in an entrained flow reactor to 1040 K. The model calculations were made using  $h_0 = 0.3$  and  $E_p = 3,000$  cal/mole.

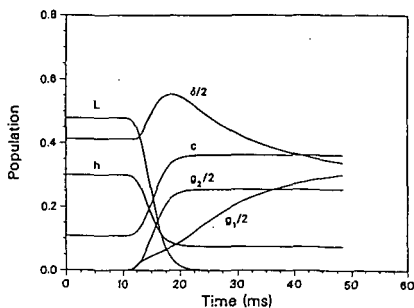


Figure 3. Predictions of dynamic variables used in the CPD model for the Illinois #6 coal,  $h_0 = 0.3$ ,  $E_p = 3000$  cal/mole. Variables  $\delta$ ,  $g_1$  and  $g_2$  are scaled by a factor of 2.

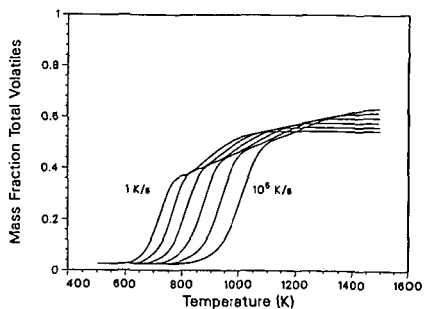


Figure 4. Predicted effect of heating rate on total volatiles yield from Illinois #6 hvb bituminous coal. Numerical experiments performed by heating at the designated rate to 1500 K (zero hold time).

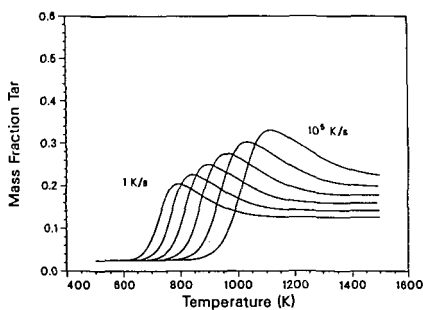


Figure 5. Predicted effect of heating rate on tar yield from Illinois #6 hvb bituminous coal. Numerical experiments performed by heating at the designated rate to 1500 K (zero hold time).

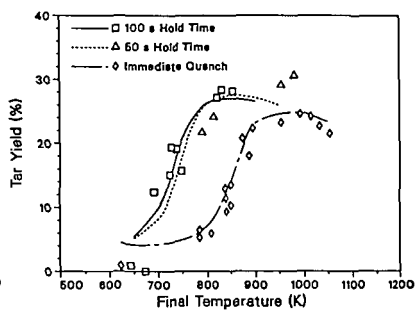


Figure 6. Comparison of CPD model calculations (curves) with Freihaut Pittsburgh #8 coal devolatilization data [10] at different hold times. Experiments were conducted by heating the coal at 1000 K/s to the final temperature and holding for 0, 50, and 100 s before quenching.